

# Energy shifts of $K$ x-ray lines for different chemical compounds of Ru, Pr, and Yb<sup>†</sup>

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The energy shifts of  $K\alpha_2$ ,  $K\alpha_1$ ,  $K\beta_3$ ,  $K\beta_1$ , and  $K\beta_2$  x rays were measured for the following Ru, Pr, and Yb compounds: Ru,  $\text{Ru}(\text{CO}_2)\text{Cl}_2$ ,  $\text{RuO}_2$ ,  $[\text{Ru}(\text{NH}_3)_4\text{OHCl}]\text{Cl} \cdot 2\text{H}_2\text{O}$ , and  $\text{RuF}_3$ ; Pr,  $\text{PrC}_2$ ,  $\text{Pr}_2\text{O}_3$ ,  $\text{PrFeO}_3$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{PrO}_2$ ,  $\text{CsPrF}_5$ , and  $\text{Cs}_2\text{PrF}_6$ ; Yb,  $\text{YbF}_3$ , and  $\text{Yb}_2\text{O}_3$ . The results are compared with free-ion relativistic self-consistent-field calculations. The measurements bear out the dominant role of the  $4f$  electrons in energy shifts between the trivalent and tetravalent Pr and the divalent and trivalent Yb. In Yb the full free-ion value is observed, while in Pr the free-ion value appears to be attenuated by a factor of 0.4, presumably owing to covalency. In all cases the relation of the x-ray energy shift to the Mössbauer isomer shift is discussed.

## I. INTRODUCTION

Chemical shifts of  $K$  x-ray transitions in medium heavy and heavy atoms have recently been receiving considerable attention. Pioneering work on finding and exploring chemical energy shifts of  $K$  x-ray lines is due to Sumbaev<sup>1</sup> and co-workers. This group has extensively studied the effects of valence electrons on the  $K$  x-ray energies in various compounds of Mo, Ag, Sn, Sb, W and in rare earths. At the same time, measurements on compounds of Sn,<sup>2</sup> and Pr<sup>3</sup> have been reported from the Cal Tech group. Interest in chemical shifts has been stimulated by the advent of modern self-consistent-field calculations. It appears possible today, from the observed energy shifts of inner atomic shells to reach conclusions regarding the configuration of the outer electrons participating in the chemical bond. The self-consistent potential not only allows the calculation of electronic eigenvalues for different free-ion configurations, but also gives predictions for the  $s$ -electron densities at the nucleus. These  $s$ -electron densities, in turn, can be compared with results from Mössbauer isomer-shift experiments. In this sense,  $K$  x-ray chemical shifts and Mössbauer isomer shifts are complementary, and provide the input for an analysis of atomic structure with a self-consistent-field program.

It is the aim of this paper to present x-ray data and discuss several aspects of the chemical electron structure for compounds of Ru, Pr, and Yb. In all three cases extensive Mössbauer studies have been reported.<sup>4-9</sup> The work on the rare earths Pr and Yb is perhaps the most interesting aspect of our paper, because the dominant role of the  $4f$  electrons is clearly borne out from the present results.

A relatively good agreement is found between the experimental data and the free-ion calculations

in Yb and Pr showing that such a simple model of the electron structure describes the eigenvalues and densities in the region of the inner shells quite well. On the other hand, the same model seems to fail in the case of Ru, a finding which is not quite unexpected. Nevertheless, the free-ion calculations have been used for comparison of the data as it appears difficult to obtain quantitative predictions from the molecular-orbital theory.

## II. EXPERIMENT

The experimental technique used to measure the  $K$  x-ray chemical shifts is very similar to that employed for the  $K$  x-ray isotope shifts which has been described in Ref. 10. In addition to the use of an x-ray tube to excite fluorescent  $K$  x-rays from the chemical samples, we have relied on a radioactive source of  $^{169}\text{Yb}$ . The spectrometer is a new version of our 2-m curved-crystal diffractometer. Some details pertaining to the spectrometer will be given below. An outline of the experimental set-up is shown in Fig. 1.

A radioactive source has the obvious advantage over an x-ray tube of ideal beam stability.  $^{169}\text{Yb}$  has a half-life of 31 days and, among other things, emits a strong 63-keV  $\gamma$  ray, which is ideal for photoexcitation of the  $1s$  shell of medium-heavy atoms up to Yb. The radioactive source was prepared by irradiating 200 mg of 20% enriched  $^{168}\text{Yb}$  in the form of  $\text{Yb}_2\text{O}_3$  mixed with 400 mg of Al powder for 15 days at a flux of  $1.1 \times 10^{14}$  n/sec  $\text{cm}^2$ . The source strength was 200 Ci. The welded source capsule is enclosed in a shielding container. A shutter at the front end of the capsule can be retracted by remote control and the capsule pushed forward close to the chemical sample.

The spectrometer, designed by Henrikson,<sup>11</sup> consisted of two separate units, a crystal pivot

unit and a movable slit. These two units placed 2 m apart rested on a massive octahedral concrete support. The fluorescent x rays from the chemical samples were Bragg refracted at the crystal in the Cauchois geometry and detected by a NaI crystal behind the slit. (See Fig. 1.)

The crystal pivot unit consisted of the bent crystal, the pivot bearing, and a screw mechanism which allowed coarse adjustment to the proper Bragg angle for the experiment. The (310) plane normal to the surface containing the crystal  $c$  axis was used. The 2-mm-thick quartz crystal was bent to a radius of 2 m.

The slit platform was mounted on two sheet springs constraining the slit to move perpendicular to the x-ray beam. The spring also served to reduce inertial effects when the slit was moved in discrete steps. The slit platform was rigidly connected to the outer part of the precision micrometer. The scan over an x-ray profile was achieved by linear motion of the slit for a fixed crystal pivot position.

The micrometer was coupled to a "Slo-syn" motor with 200 steps/rev. Eight steps constituted a linear movement of the slit of 0.001 in (0.025 mm). The movement of the slit is linearly related to the change in wavelength in mxu (milli-x-units) by

$$\delta\lambda(\text{mxu}) = \frac{2d}{D} \delta x = 3.0 \times 10^{-4} \delta x(\text{in.})$$

where  $d = 1177.6 \text{ xu}^{12}$  is the lattice spacing of the (310) plane of quartz and  $D = 200 \text{ cm}$  is the diameter of the Rowland circle of the spectrometer.

Most of the Ru, Pr, and Yb compounds were the purest obtainable commercially.  $\text{PrO}_2$  was kindly supplied by Professor Eyring of Arizona University. The  $\text{CsPrF}_6$  and  $\text{Cs}_2\text{PrF}_6$  were obtained from Dr. F. Wagner, Technical University, Munich (Germany). Owing to the instability against

decomposition our results obtained from the latter compounds were not entirely conclusive and should be considered lower bounds. The considerable absorption by the Cs atoms further complicated the analysis.

The samples were prepared in the same way as in x-ray isotope-shift experiments of Ref. 13. The compound was mixed with Formvar powder and pressed to form a pill of optimum thickness. The pill was sandwiched between two beryllium plates and placed in a holder. Up to four such holders could be mounted in the sample wheel. The sample wheel was coupled to a stepping motor which permitted sequential exposure of the samples to the  $^{169}\text{Yb}$  source. The sample positions were recorded by means of an encoder during the experiment.

The x-ray line was scanned in steps of 30–50 mxu. At each spectrometer position, the fluorescent x rays from all compounds were counted in succession for a period of 20 sec. The sample wheel returned to the first compound for another measurement. At the end of the scan, the spectrometer returned to the starting position and the process was repeated.

Data from four successive scans were grouped to form a data unit. In the cases of  $K\alpha_1$ ,  $K\alpha_2$ , and  $K\beta_2$ , the data unit was fitted with a five-parameter Gaussian with a sloping background using a least-squares program. The five parameters were peak height, half-width, peak center, background, and slope of background.

In case of the close-lying  $K\beta_1$  and  $K\beta_3$  lines, complications in the analysis arose from the overlap of the Lorentzian tails of the two lines. In earlier experiments on  $\text{Pr}^3$  the  $K\beta_1$  and  $K\beta_3$  lines were measured separately and differences in the chemical shifts were found. In the present measurement the two lines were scanned together in a single run and the data was fitted to an eight-parameter least-squares fit (two Lorentzians with common background and slope) as well as to a nine-parameter fit (including a parabolic background). Again different shifts were observed for the  $K\beta_1$  and  $K\beta_3$  lines depending on the fitting function. Further analysis showed that these differences of the centroid shifts were correlated to the relative intensities of the two lines which varied by 1 to 2% for the different compounds, presumably owing to different relative absorption in the target. However, it was found that the shift of the center of gravity of the combined  $K\beta_1$  and  $K\beta_3$  lines remained unchanged for different fitting functions or slightly varying intensity ratios. The centroid shift of the combined  $K\beta_1$  and  $K\beta_3$  line was therefore considered to be the relevant parameter for comparison with theory.

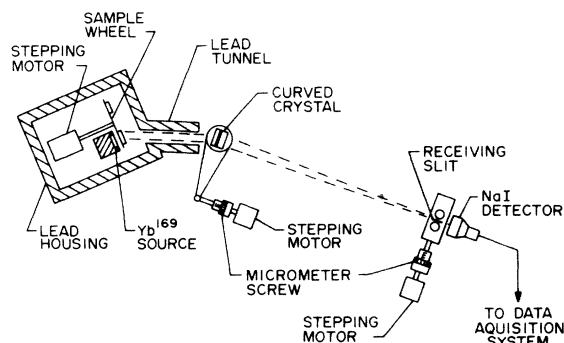


FIG. 1. Experimental arrangement for x-ray-shift measurements.

TABLE I. Observed chemical shifts in Ru compounds.  $\Delta E = E(A) - E(B)$  in meV.

x-ray line	A Ru-Ru(CO) <sub>2</sub> Cl <sub>2</sub>	B Ru-RuO <sub>2</sub>	A Ru-RuF <sub>3</sub>	B Ru-[Ru(NH <sub>3</sub> ) <sub>4</sub> OHCl]Cl·2H <sub>2</sub> O
$K\alpha_2$	+17 ± 10	-11 ± 10	-53 ± 10	...
$K\alpha_1$	-18 ± 4	-42 ± 4	-94 ± 3	-5 ± 6
$K\beta_2$	...	+24 ± 25	+50 ± 25	+31 ± 25

## III. RESULTS OF EXPERIMENTS

The results of the  $K\alpha_1$ ,  $K\alpha_2$ ,  $K\beta_{1,3}$ , and  $K\beta_2$  chemical shifts in Ru, Pr, and Yb are presented in Tables I, II, and III, respectively. In Ru the chemical shifts are displayed with respect to the Ru metal. In Pr the reference compound is  $\text{PrF}_3$ .

Comparisons with the work of Sumbaev<sup>1</sup> are possible for several compounds. Sumbaev and co-workers have measured the  $K\alpha_1$  line only and a comparison of our data with Sumbaev's data (given in parenthesis) shows good agreement for the following pairs:

Pr- $\text{Pr}_2\text{O}_3$ :  $50 \pm 9$  ( $20 \pm 15$ ) meV;

Pr- $\text{Pr}_6\text{O}_{11}$ :  $272 \pm 6$  ( $263 \pm 9$ ) meV;

Yb- $\text{Yb}_2\text{O}_3$ :  $592 \pm 26$  ( $582 \pm 30$ ) meV;

Yb- $\text{YbF}_3$ :  $579 \pm 26$  ( $557 \pm 27$ ) meV.

Our earlier Pr data<sup>3</sup> have been included in the present data.

## IV. RESULTS OF CALCULATIONS

The free-ion, relativistic Hartree-Fock-Slater method was used for calculation of the  $K$  x-ray shifts,  $1s$ -electron binding energies, and the electron densities at the origin. The finite nuclear size, the vacuum polarization, and the Latter approximation, assuring correct asymptotic behavior of the self-consistent potential, were included in the calculations.

The numerical results are collected in Tables IV-VI. All quantities are calculated with respect

to the simplest trivalent configuration for each of the considered atoms. Two variants of the local exchange interaction are listed: The full free-electron-gas exchange potential was used for the upper entry; its strength was reduced by  $\frac{1}{3}$  for the lower entry. The valence electrons are less bound and further away from the core, when the exchange strength is reduced; therefore the calculated shifts (and  $\Delta D$ ) are generally smaller in the absolute value for the  $\frac{2}{3}$  exchange strength. The differences of the two variants might serve as an indicator of the uncertainty involved in the approximate treatment of the exchange electron interaction. Our calculations overlap in several cases with those by Seltzer and co-workers,<sup>3,5</sup> Raff,<sup>14</sup> and Fricke.<sup>15</sup> The agreement is generally good but, with the latter two references, not perfect. The theoretical results quoted by Sumbaev *et al.*<sup>16</sup> agree with ours in the sign and general pattern, but often differ substantially in the numerical value. The chemical shifts in Eu, calculated by Sumbaev *et al.*<sup>16</sup> and by Raff<sup>14</sup> can be compared with our results. The corresponding configurations are  $(4f)^7(6s)^1 - (4f)^6(6s)^1$  in our calculations (full exchange) and in Ref. 14, and  $(4f)^7(6s)^2 - (4f)^6(6s)^2$  in Ref. 16. The calculated  $\Delta K\alpha_2$ ,  $\Delta K\alpha_1$ ,  $\Delta K\beta_{1,3}$ ,  $\Delta K\beta_2$  shifts in meV are 660, 727, 1723, 825 in our calculations; 563, 620, 1483, 331 in Ref. 14; and 605, 671, 1671, 852 in Ref. 16. Note the over-all agreement, but the sharp disagreement in  $\Delta K\beta_2$  with Ref. 14.

In the rare-earth atoms, the  $K$  x-ray energies depend sensitively on the number of  $4f$  electrons and are much less sensitive to the  $5d$  and particu-

TABLE II. Observed chemical shifts in Pr compounds, measured with respect to  $\text{PrF}_3$ .  $\Delta E = E(\text{PrF}_3) - E(\text{compound})$  in meV.

x-ray line	Pr	$\text{PrC}_2$	$\text{Pr}_2\text{O}_3$	$\text{PrFeO}_3$	$\text{Pr}_6\text{O}_{11}$	$\text{PrO}_2$	$\text{CsPrF}_6$	$\text{Cs}_2\text{PrF}_6$	Calculation $0.4[(4f)^2 - (4f)^1]$
$K\alpha_2$		- 5 ± 10	48 ± 6		214 ± 8	320 ± 5	> 326 ± 13	> 335 ± 14	350
$K\alpha_1$	-45 ± 4	-18 ± 5	5 ± 8	94 ± 4	227 ± 5	371 ± 3			382
$K\beta_{1,3}$	-55 ± 7		11 ± 10	309 ± 7		1018 ± 4			923
$K\beta_2$	-48 ± 29		31 ± 9	127 ± 35		416 ± 18			199

TABLE III. Observed chemical shift in Yb compounds.  $\Delta E = E(A) - E(B)$  in meV.

x-ray line	$A$ Yb - YbF <sub>3</sub>	$B$ YbF <sub>3</sub> - Yb <sub>2</sub> O <sub>3</sub>	$A$ Yb - Yb <sub>2</sub> O <sub>3</sub>	Calculation ( $4f$ ) <sup>14</sup> - ( $4f$ ) <sup>13</sup>
$K\alpha_2$	570 ± 114	-5 ± 15	564 ± 15	562
$K\alpha_1$	579 ± 26	13 ± 16	592 ± 26	635
$K\beta_{1,3}$	1402 ± 43	275 ± 71	1676 ± 62	1465
$K\beta_2$	586 ± 114	253 ± 110	839 ± 119	908

larly to the 6s and 6p electrons. The quantity  $\Delta D$ , the difference of electron density at the nucleus (measured in the Mössbauer isomer shifts), depends critically on both 4f and 6s electrons; the removal of one 4f electron or the addition of one 6s electron increases the  $\Delta D$  by roughly the same amount. In the transitional metal  $_{44}\text{Ru}$ , the distinction between the different electron orbits is less pronounced. The 4d electrons are primarily responsible for the chemical shifts, while 5s electrons determine the change in the density  $D$ . As can be easily seen from the tables, the effect of different electrons is always only approximately additive (for example, the  $\Delta K\alpha_1$  caused by the removal of one 4d electron in Ru depends on the total number of 4d electrons present, the  $\Delta D$  depends on the spectator 5s electrons, (etc.)).

In Sumbaev's analysis<sup>1,16</sup> it is assumed that the shifts corresponding to the removal of one electron depend only on the quantum state of the electron, but are independent on  $Z$  and on its ionization state. According to our calculations, this is a rather crude approximation. Figure 2 demonstrates this conclusion; it shows how the  $\Delta K$  shifts corresponding to the removal of one 4f electron depend on the total number of 4f electrons present. None of the lines in Fig. 2 is par-

allel to the abscissa axis; they are not even parallel to each other.

The calculations thus show that perfect one-to-one correspondence between the chemical and isomer shifts cannot be expected. The states of the valence electrons in real compounds are certainly poorly described by the free-ion solution. However, assuming that the real molecular orbits are linear combinations of the atomic orbits and noticing the general features discussed above, we can give a qualitative interpretation of the measured chemical shifts.

## V. DISCUSSION

### A. Ruthenium

The measured chemical shifts in the compounds of Ru are shown in Table I, while the free-ion calculated values are collected in Table IV. It is very difficult to see much correspondence between experiment and any set of calculations in Table IV. It may be noted, however, that both the observed shifts and those calculated for 4d electrons reflect a sign change for  $\Delta K\alpha_{1,2}$  and  $\Delta K\beta_2$ . The measured shifts are much smaller than the calculated ones, and are not proportional to them.<sup>17</sup>

The Mössbauer isomer shifts in a number of Ru

TABLE IV. Ionic configurations of  $_{44}\text{Ru}$ . For each quantity in the first column, the differences between the values for a configuration, given in the first line, and for the trivalent (4d)<sup>5</sup> configuration are shown. The upper and lower value listed for each quantity corresponds respectively to the full and  $\frac{2}{3}$  strength of the exchange interaction as discussed in the text. The  $\Delta E_{1s}$  is the difference of the 1s-electron energies, the  $\Delta K_x$  is the shift in the corresponding K x-ray energy, all in meV. The  $\Delta D$ , the difference of the electron density at the origin, is in 10<sup>26</sup> cm<sup>-3</sup>.

	(4d) <sup>6</sup>	(4d) <sup>6</sup> (5s) <sup>1</sup>	(4d) <sup>5</sup> (5s) <sup>1</sup>	(4d) <sup>4</sup>	(4d) <sup>4</sup> (5s) <sup>1</sup>	(4d) <sup>4</sup> (5p) <sup>1</sup>	(4d) <sup>3</sup>	(4d) <sup>2</sup>
$\Delta E_{1s\ 1/2}$	16 274	26 082	11 097	-18 077	-5839	-6836	-37 924	-59 313
	14 855	24 360	10 932	-16 792	-4624	-5478	-35 428	-55 693
$\Delta K\alpha_2$	213	154	-86	-252	-359	-359	-519	-819
	155	115	-90	-205	-330	-330	-462	-744
$\Delta K\alpha_1$	218	157	-88	-254	-359	-367	-525	-826
	158	117	-95	-208	-338	-338	-469	-754
	25	-55	-142	+70	-140	-171	289	661
$\Delta K\beta_{1,3}$	-15	-112	-197	+83	-207	-242	267	587
	-1170	-1378	-415	1745	1070	1080	4150	7170
$\Delta K\beta_2$	-890	-1204	-546	1355	580	542	3270	5740
	-0.35	0.95	1.7	0.46	2.5	0.37	1.05	1.77
$\Delta D$	-0.20	0.73	1.3	0.31	2.0	0.25	0.81	1.38

TABLE V. Free-ion configurations of  $_{59}\text{Pr}$ . Columns 2-5 give, for each quantity in lines 2-11, the differences in energy corresponding to the  $(4f)^2$  configuration minus the energy of the configuration in first line, while columns 6-11 give the energy differences of the  $(4f)^1$  configuration minus the configuration in the first line. Lines 12 and 13 give the corresponding changes in density. The symbols and units are explained in the caption to Table IV.

	$(4f)^3$	$(4f)^2(6s)^1$	$(4f)^1$	$(4f)^0$	$(4f)^1(6s)^2$	$(4f)^1(6s)^1$	$(4f)^1(6s)^1(5d)^1$	$(4f)^1(5d)^1$	$(4f)^0(6s)^1$	$(4f)^0(5d)^1$
$\Delta E_{s1/2}$	-19 053 -16 529	-8699 -8762	21 743 19 923	45 755 42 419	-18 575 -18 094	-9711 -9758	-21 927 -20 913	-13 141 -13 403	13 368 11 797	9498 8760
$\Delta K\alpha_2$	-729 -561	-1 -1	875 760	1876 1646	29 10	30 28	-164 -141	-164 -127	1045 873	806 741
$\Delta K\alpha_1$	-794 -611	2 2	956 823	2050 1800	33 22	33 38	-166 -133	-167 -124	1149 1067	895 827
$\Delta K\beta_{1,3}$	-1932 -1527	42 61	2307 2086	4921 4549	120 120	89 108	-6 14	-46 -12	2654 2643	2582 2463
$\Delta K\beta_2$	-735 -780	107 167	497 737	672 1229	301 341	193 341	276 295	176 178	433 879	490 804
$\Delta D$	2.10 1.61	-2.20 -1.81	-2.67 -2.31	-5.88 -5.04	-5.10 -4.11	-2.87 -2.38	-1.73 -1.47	0.53 0.37	-6.60 -5.75	-2.38 -2.14

compounds were analyzed in Refs. 4 and 5. Our chemical  $\Delta K\alpha_1$  shifts can be contrasted to the Mössbauer isomer shifts with the help of Fig. 3. Both shifts are shown with respect to Ru metal. The scales are arbitrarily adjusted so that the observed values for  $\Delta E$  ( $\text{RuF}_3$ ) and  $\Delta D$  ( $\text{RuBr}_3$ ) line up horizontally. An average value of  $\delta\langle r^2 \rangle = 2.5 \times 10^{-2} \text{ fm}^2$  has been used for the 90-keV transition in  $^{99}\text{Ru}$ . It can be seen that the chemical and isomer shifts have the same ordering. (The points are related with nearly horizontal dashed lines.) The absolute values of the chemical shifts are roughly five times smaller than the calculation (Table IV) assuming  $(4d)^n$  configurations. Likewise, the  $\Delta D$  appears about two times smaller than the calculated value.

A crude estimate of the  $\delta\langle r^2 \rangle \approx 14 \times 10^{-2} \text{ fm}^2$ , based on a simple nuclear model, is quoted in Ref. 5. Using this larger  $\delta\langle r^2 \rangle$  the  $\Delta D$  is reduced about 11 times with respect to the calculated value. Thus, similar trends exist in both  $\Delta E$  and  $\Delta D$ .

The electron configurations quoted in Fig. 3 for comparison with theory are based on the observed ordering of Mössbauer isomer shifts and assignments by Kaendl *et al.*<sup>4</sup> According to the isomer shifts, the Ru metal behaves as if it has the ionization state 5+ and, consequently, the electron configuration  $(4d)^5$ . Similarly, the divalent compound  $\text{Ru}(\text{CO})_2\text{Cl}_2$  has the isomer shift corresponding to the  $(4d)^4$  configuration.

#### B. Praseodymium

A comparison between experiment (Table II) and calculation (Table V) reveals several interesting aspects.

We observe that the trivalent compound  $\text{Pr}_2\text{O}_3$  and Pr metal show a very small chemical shift with respect to  $\text{PrF}_3$  for all the K x-rays. The observed shift of the order of 10-50 meV can be attributed to a 6s or 6p electron. The small shift in  $\text{PrC}_2$  makes this compound appear trivalent.

The tetravalent compound  $\text{PrO}_2$ , on the other hand, shows a large shift. The latter can only be due to a 4f electron. The observed relative shifts of  $K\alpha_2/K\alpha_1$ ,  $K\beta_{1,3}/K\alpha_1$ , and  $K\beta_2/K\alpha_1$  in  $\text{PrO}_2$  amount to 0.86, 2.75, and 1.12, respectively. The corresponding calculated shifts for  $(4f)^1-(4f)^2$  using full ( $\frac{2}{3}$  full) exchange strength are 0.915 (0.923), 2.41 (2.53), and 0.52 (0.90), respectively.  $K\beta_2$  transition is rather sensitive to the exchange strength, as well as to the presence of a 6s electron. Fair agreement between experiment and calculation can be achieved for all x-ray ratios by adjusting exchange strength or 6s population. The absolute value of the shift for  $\text{PrO}_2$ , however,

TABLE VI. Free-ion configurations in  $_{70}\text{Yb}$ . For each quantity shown in column 1, lines 2–11 give the differences in energy associated with the configuration listed in the first line minus the energy of the  $(4f)^{13}$  configuration. Lines 12 and 13 give the corresponding changes in density. The symbols and units are explained in Table IV.

	$(4f)^{14}$	$(4f)^{14}(6s)^1$	$(4f)^{14}(5d)^1$	$(4f)^{13}(6s)^1$	$(4f)^{13}(6p)^1$	$(4f)^{13}(5d)^1$	$(4f)^{13}(6s)^1(5d)^1$	$(4f)^{12}$
$\Delta E_{1s\frac{1}{2}}$	20 625	29 246	31 015	9844	8694	12 782	21 347	-23 361
	17 977	26 587	27 180	9947	9010	11 788	19 948	-21 259
$\Delta K\alpha_2$	562	580	650	0	8	104	122	-671
	433	468	511	-14	-9	65	73	-560
$\Delta K\alpha_1$	635	650	722	-5	4	103	119	-761
	488	520	562	-20	-15	63	79	-633
$\Delta K\beta_{1,3}$	1465	1430	1466	-66	-55	-34	-46	-1762
	1140	1102	1120	-97	-88	-59	-84	-1505
$\Delta K\beta_2$	908	876	958	-70	-68	-7	-11	-803
	857	800	870	-137	-141	-66	-103	-930
$\Delta D$	-3.7	-0.4	-4.0	4.9	0.3	-0.5	3.3	4.8
	-2.8	-0.1	-2.6	4.1	0.2	-0.2	2.9	3.9

does not appear to agree with any of the configurations involving  $4f$  listed in Table V. To fit the data for all  $K$  x rays one needs one single scaling factor of about 0.4, as seen in Table II.

If  $\text{PrF}_3$  is truly ionic trivalent with a configuration  $(4f)^2$ , then it must be concluded that  $\text{PrO}_2$  possesses a "configuration" of  $(4f)^{1.6}$ , the addi-

tional 0.6 electrons being attributable to covalency. It should be pointed out, however, that chemical shifts are rather insensitive to additional contributions of  $6s$  electrons.

For  $\text{PrFeO}_3$  the ratios are  $K\beta_{1,3}/K\alpha_1 = 3.28$ ,  $K\beta_2/K\alpha_1 = 1.35$ , again characteristic for a change in  $4f$  configuration. The common scaling factor is 0.1 and this compound can be assigned a configuration  $(4f)^{1.9}$  with large covalency. Similarly,  $\text{Pr}_6\text{O}_{11}$  can be assigned  $(4f)^{1.75}$  and  $\text{CsPrF}_5$  as well as  $\text{Cs}_2\text{PrF}_6$  have  $(4f)^{1.6}$ .

A comparison with the Mössbauer isomer shifts is possible. The isomer shift reflects the change

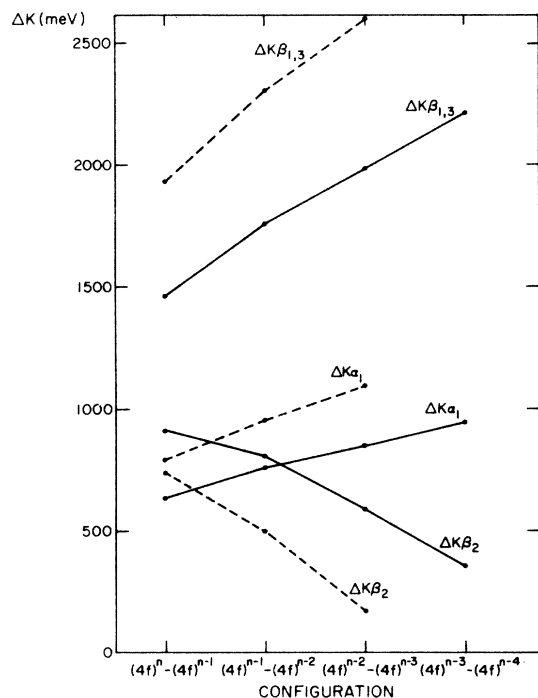


FIG. 2. Dependence of  $K$  x-ray energy shifts, corresponding to removal of one  $4f$  electron, on the number of spectator  $4f$  electrons. The shifts were calculated for  $_{70}\text{Yb}$  (solid line,  $n=14$ ), and  $_{59}\text{Pr}$  (dashed line,  $n=3$ ). The involved configurations are shown at the bottom line;  $n$  is the number of  $4f$  electrons in a normal atom. All shifts are in units of meV.

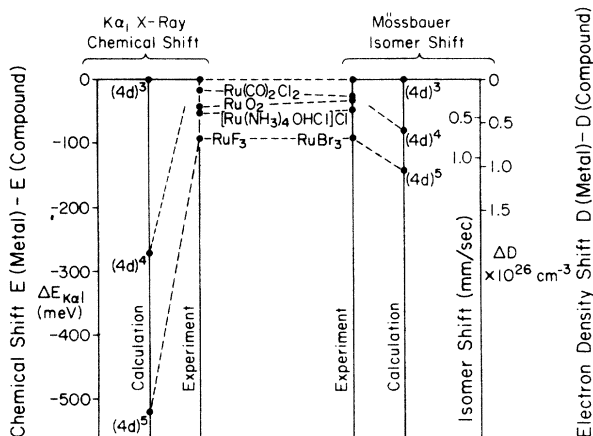


FIG. 3. Comparison of  $K\alpha_1$  x-ray chemical shift and Mössbauer isomer shifts of the 90-keV  $\gamma$  ray in compounds of  $_{99}\text{Ru}$ . The shifts are shown with respect to  $\text{Ru}$  metal. The scales are arbitrarily related to each other so that the observed chemical shift for  $\text{RuF}_3$  and the isomer shift for  $\text{RuBr}_3$  line up horizontally. The calculated chemical shifts (Table IV) are for the configurations  $(4d)^3 - (4d)^5$  and  $(4d)^3 - (4d)^4$ . The calculated  $\Delta D$  (Table IV) are for the same configurations. The experimental  $\Delta D$  are from Ref. 4 with the assumption of  $\delta\langle r^2 \rangle = 2.5 \times 10^{-2} \text{ fm}^2$  quoted in Ref. 5.

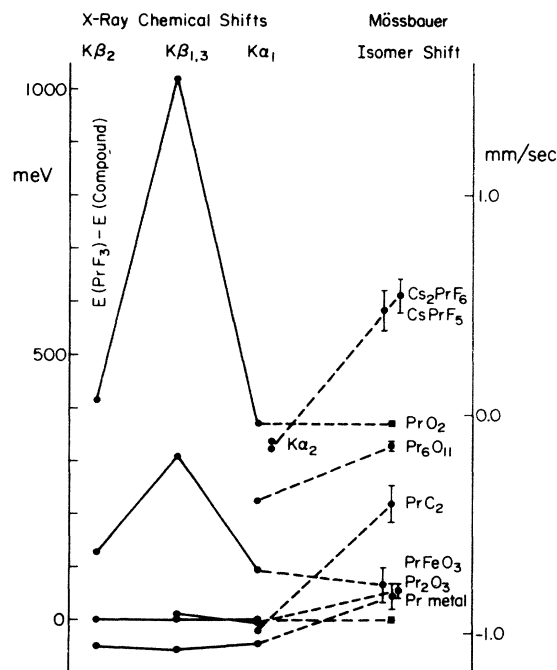


FIG. 4. Comparison of x-ray chemical shifts and Mössbauer isomer shift in Pr compounds.  $\text{PrF}_3$  was chosen as a reference for all three x rays and thus determines a base line. The scale for the x-ray shift is normalized so that the  $K\alpha_1$  x ray for  $\text{PrO}_2$  is on the same horizontal line as the  $\text{PrO}_2$  isomer shift. The Mössbauer shifts (Ref. 4) are measured with respect to Pr in  $\text{CeO}_2$ .

of the electron density at the nucleus. Bent *et al.*,<sup>7</sup> Kapfhammer *et al.*,<sup>8</sup> and Groves *et al.*<sup>9</sup> have reported isomer shifts in  $^{141}\text{Pr}$  for several chemical compounds, many of them identical with those used here. Figure 4 shows a comparison between the present x-ray data and the isomer-shift data of Kapfhammer *et al.*<sup>8</sup> The ordinate scale for the Mössbauer data, representing the Doppler velocity needed to restore nuclear resonance, is proportional to the differences in electron density at the nucleus. The scale has been arranged for comparison with the x-ray data, to horizontally line up  $K\alpha_1$  and isomer-shift data points for  $\text{PrF}_3$  and  $\text{PrO}_2$ .

For Pr metal and  $\text{PrC}_2$  the comparison suggests

that the  $4f$  configuration is unchanged, compared to  $\text{PrF}_3$ , but that Pr metal and  $\text{PrC}_2$  contain some  $6s$  electrons, which increase the Mössbauer shift and decrease the x-ray shift, as borne out in Table II.

### C. Ytterbium

The measured chemical shifts in Yb are shown in Table III; the calculated free-ion values for removal of one  $4f$  electron are shown in the last column. The agreement of the experimental and calculated values is surprisingly good. Inspection of Table VI, where all calculated free-ion shifts are collected, leaves no doubt that the shifts between Yb metal and trivalent Yb are really caused by removal of one  $4f$  electron.

The experimental  $\text{YbF}_3$ - $\text{Yb}_2\text{O}_3$  shifts are much smaller; thus the  $4f$  electron configurations must be identical in both compounds. The  $5d$  electrons do not contribute apparently either, because  $K\alpha$  x rays are not shifted. The pattern of the  $\text{YbF}_3$ - $\text{Yb}_2\text{O}_3$  shifts resembles the effect of  $6s$  or  $6p$  electrons (see columns 5 and 6 in Table VI); they are, however, 3 to 4 times larger than the calculated ones. To further explore these details it is necessary to understand the molecular orbits involved.

Mössbauer isomer shifts were measured in a number of Yb compounds.<sup>9</sup> The isomer shifts between Yb metal and the trivalent compounds are considerably smaller than the shifts between the bivalent  $\text{YbSO}_4$  and trivalent Yb. Such a decrease in isomer shift can be attributed to the charge density of conduction electrons, which according to Ref. 18, equals 45% of the  $\Delta D$  ( $\text{Yb}^{3+}$ - $\text{Yb}^{2+}$ ). Our chemical shift results show that  $4f$  electrons do not participate in the conduction band, in agreement with Gschneidner.<sup>19</sup>

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